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Supplementary Information for

Formation of carbon propeller-like molecules from starphenes under electron irradiation

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Simulated structure evolution during the carbon propeller-like molecule formation from the $C_{54}H_{30}$ starphene in vacuum under 45 keV electron irradiation in HRTEM

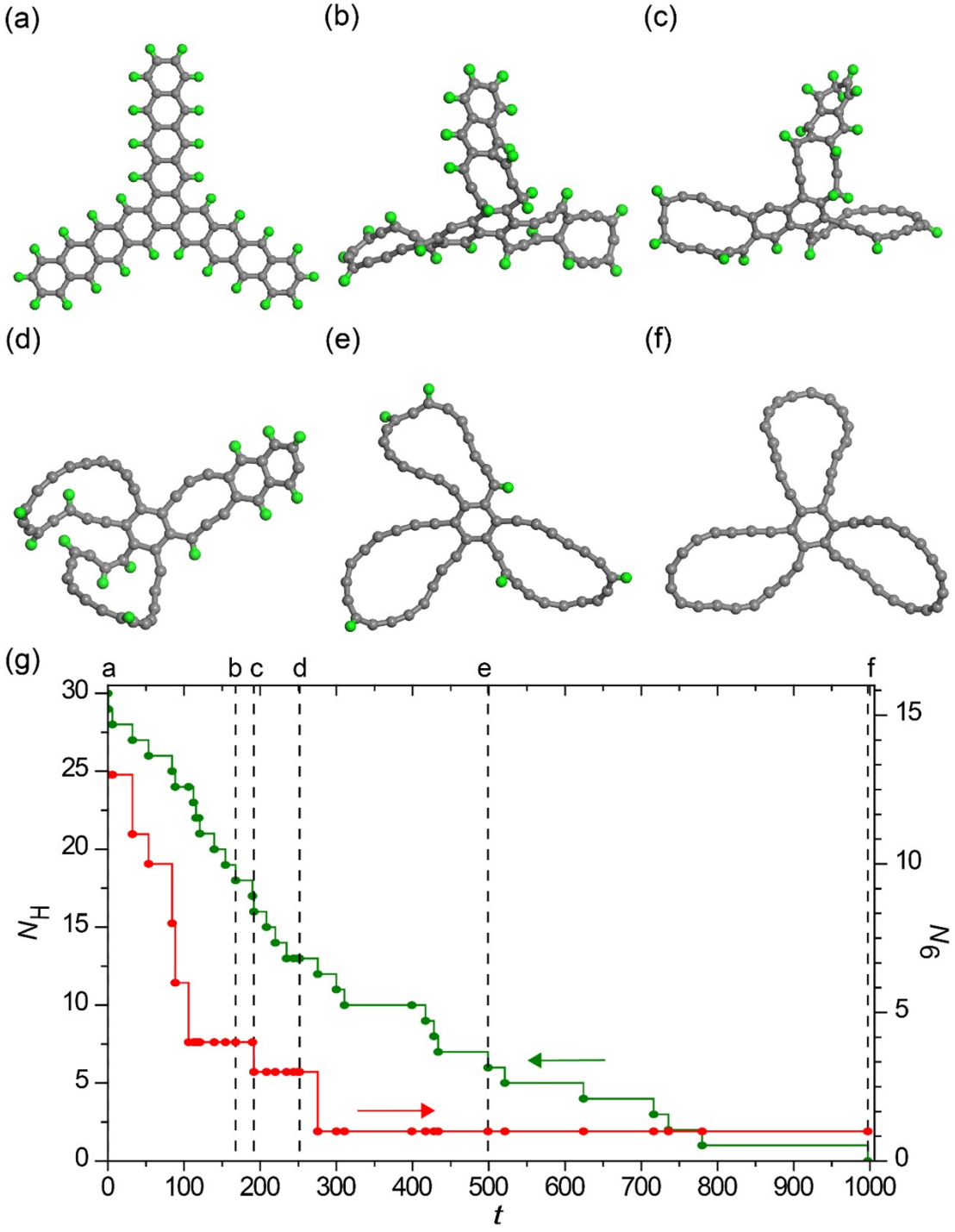


Figure S1. (a)–(f) Simulated structure evolution during the carbon propeller-like molecule formation from the $C_{54}H_{30}$ starphene in vacuum under irradiation electrons with the kinetic energy 45 keV in HRTEM: (a) 0 s, (b) 167.7 s, (c) 191.5 s, (d) 251.6 s, (e) 498.9 s and (f) 997.1. s. The direction of the electron beam is out of the page. Carbon and hydrogen atoms are colored grey and green, respectively. The atomic structure of the graphene substrate is shown by grey lines. (g) Calculated number of hydrogen atoms in the molecule, N_H (green line), and number of hexagons in the molecule structure, N_6 (red line), as functions of time t in the same simulation run. The moments of time corresponding to structures (a)–(f) are shown by vertical dashed lines.

Simulated structure evolution during the carbon propeller-like molecule formation from the $C_{54}H_{30}$ starphene in vacuum under 80 keV electron irradiation in HRTEM

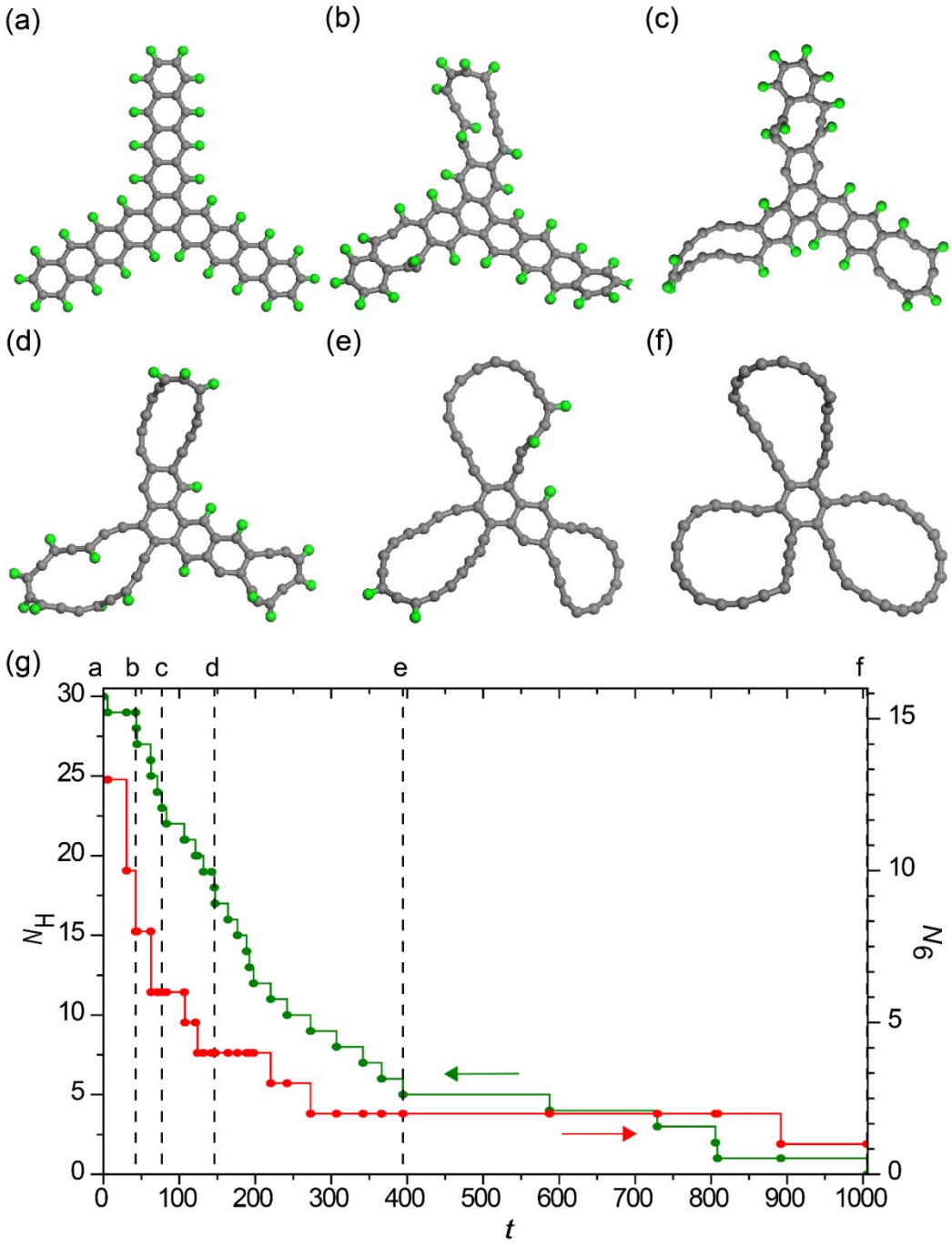


Figure S2. (a)–(f) Simulated structure evolution during the carbon propeller-like molecule formation from the $C_{54}H_{30}$ starphene in vacuum under irradiation electrons with the kinetic energy 80 keV in HRTEM: (a) 0 s, (b) 42.2 s, (c) 77.0 s, (d) 145.9 s, (e) 394.1 s and (f) 1005.2 s. The direction of the electron beam is out of the page. Carbon and hydrogen atoms are colored grey and green, respectively. The atomic structure of the graphene substrate is shown by grey lines. (g) Calculated number of hydrogen atoms in the molecule, N_H (green line), and number of hexagons in the molecule structure, N_6 (red line), as functions of time t in the same simulation run. The moments of time corresponding to structures (a)–(f) are shown by vertical dashed lines.

Examples of other molecules obtained in MD simulations

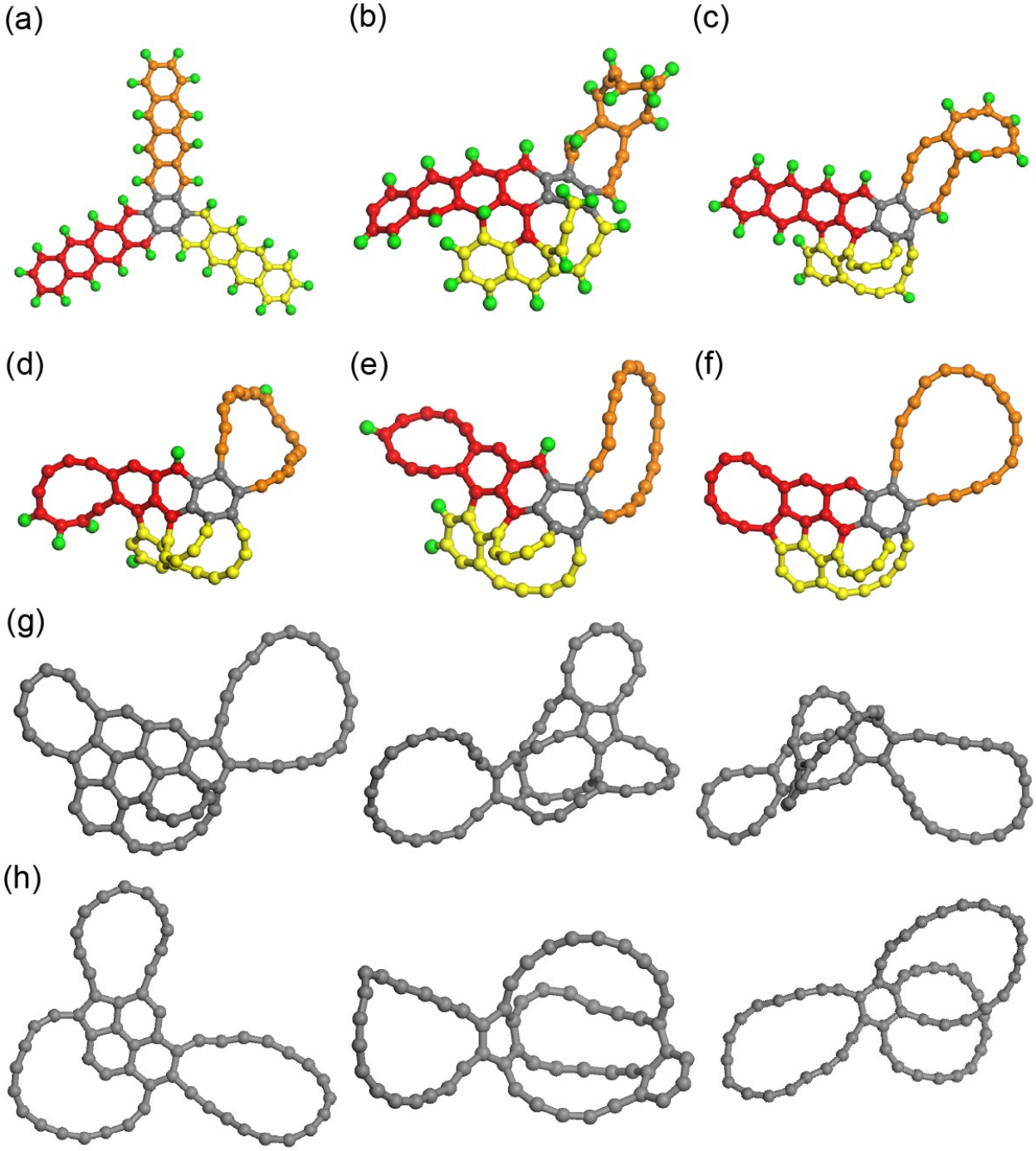
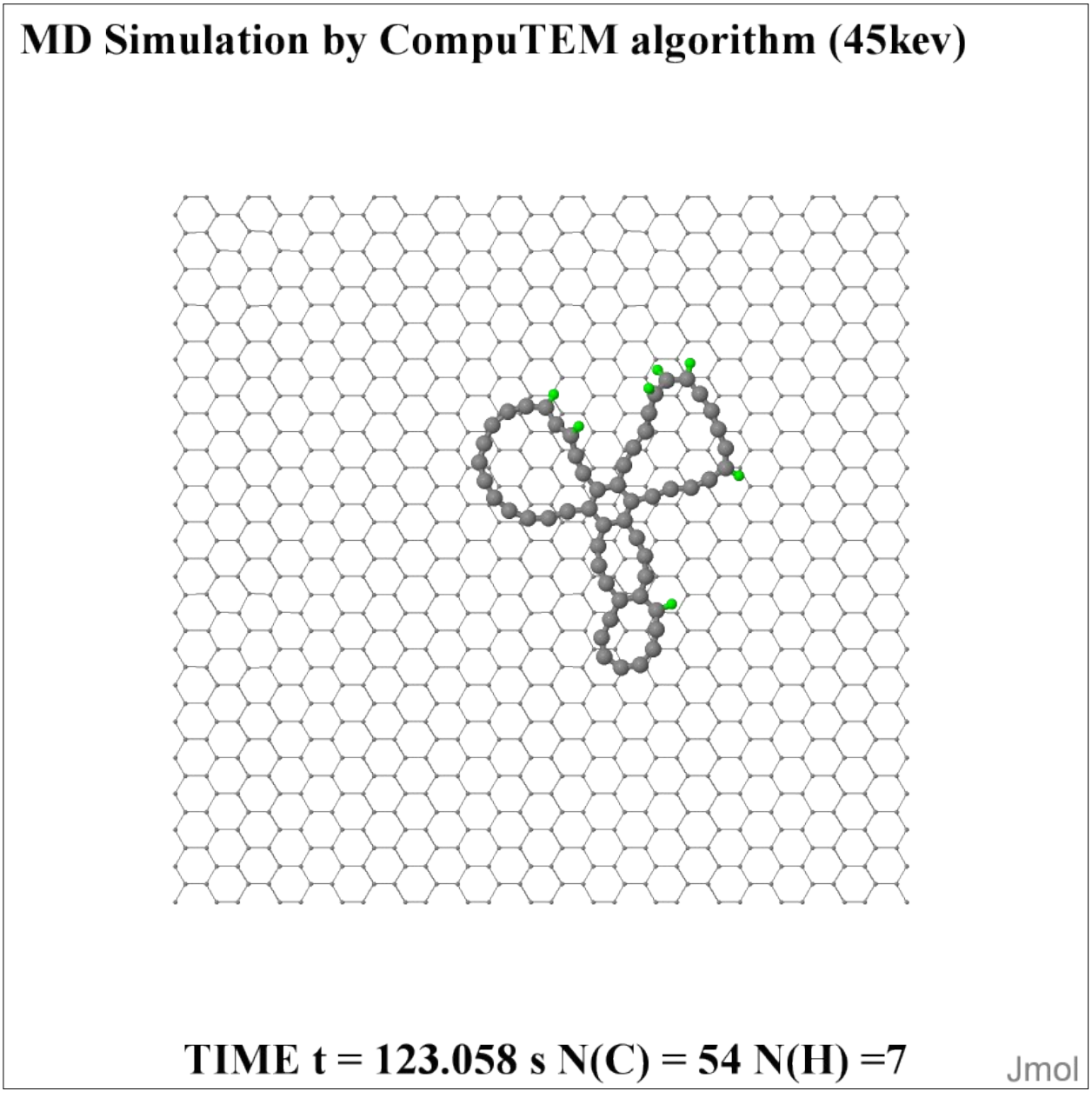


Figure S3. (a)–(f) Simulated structure evolution during the other molecule formation from the $C_{54}H_{30}$ starphene in vacuum under irradiation electrons with the kinetic energy 45 keV in HRTEM.: (a) 0 s, (b) 33.2 s, (c) 128.8 s, (d) 425.6 s, (e) 524.3 s and (f) 1055.7 s. Three different arms of the initial starphene molecule are colored red, yellow and orange, respectively, hydrogen atoms are colored green. Examples of other molecules formed after transformation of the starphene molecule under (g) 45 keV and (h) 80 keV electron irradiation in vacuum.

Description of the video file attached

Video file “vid_star_graphene_45kev.mp4” shows an example of the structure evolution observed in the MD simulations during the carbon propeller-like molecule formation from the $C_{54}H_{30}$ starphene on the graphene surface in HRTEM under electron irradiation with the electron kinetic energy of 45 keV. In this video, all carbon and hydrogen atoms are colored in grey and green, respectively. The total time in HRTEM (converted from the MD simulation time) is given at the bottom of the frame.



Energetics of molecules based on the carbon propeller-like molecule: comparison between REBO-1990EVC_CH and REBO-2002 potentials and DFT

To check the adequacy of the REBO-1990EVC_CH potential[S1] used in our MD simulations, we compared the relative energies of the molecules related to the carbon propeller-like molecule A (CPLM A). All the considered molecules are given in Figure S4. Molecules with additional bonds within and between atomic chains that are unstable according to the DFT calculations are marked as U1-U7. Metastable CPLM-based molecules with additional bonds within atomic chains are marked as I1-I7. Molecules with bonds between the first atoms of neighbor atomic chains of the CPLM are marked as B4-D4, molecules with bonds the first and second atoms are marked as B5-D5. Formation energies of stable molecules relative to the energy of CPLM A are given in Table S1. Barriers for transitions between CPLM A and molecules B4-D4 as well as molecules B5-D5 are listed in Table S2 (see the schematic representation of the pathways in Figure 2c). For comparison, we also repeated these calculations using the second-generation Brenner potential (REBO-2002).[S2]

The data presented in Tables S1 and S2 demonstrate that the potential REBO-1990EVC_CH used for the present study reproduces the main features related with the CPLM formation which follow from the DFT calculations: 1) the huge energy release of the transformation of the starphene molecule after hydrogen removal into the CPLM and 2) the stability of the CPLM relative to the formation of new bonds between and within chains after the synthesis. Note that the REBO-2002 potential does not describe these features.

REBO-1990EVC_CH properly describes the huge relative energy of the starphene molecule after complete hydrogen removal (U1) compared to the CPLM A (different from REBO-2002). It gives reasonable energies for metastable structures I from Figure 2b with bonds within the chains. Although it predicts that some unstable structures U from Figure 2a are metastable, their energies are considerably higher than that of the CPLM A (note that according to REBO-2002, some of these structures are more stable than CPLM A). Also REBO-1990EVC_CH is not only qualitatively but also quantitatively correct in the description of the energies of the structures along the upper pathway of Figure 2c (B5, C5 and D5) related to formation of pentagons in CPLM A. Both REBO-1990EVC_CH and REBO-2002 potentials overestimate the energies of the along the lower pathway of Figure 2c (B4, C4 and D4) related to the formation of tetragons in CPLM A. Further refining of the potential parameters is needed to improve the description of such rings.

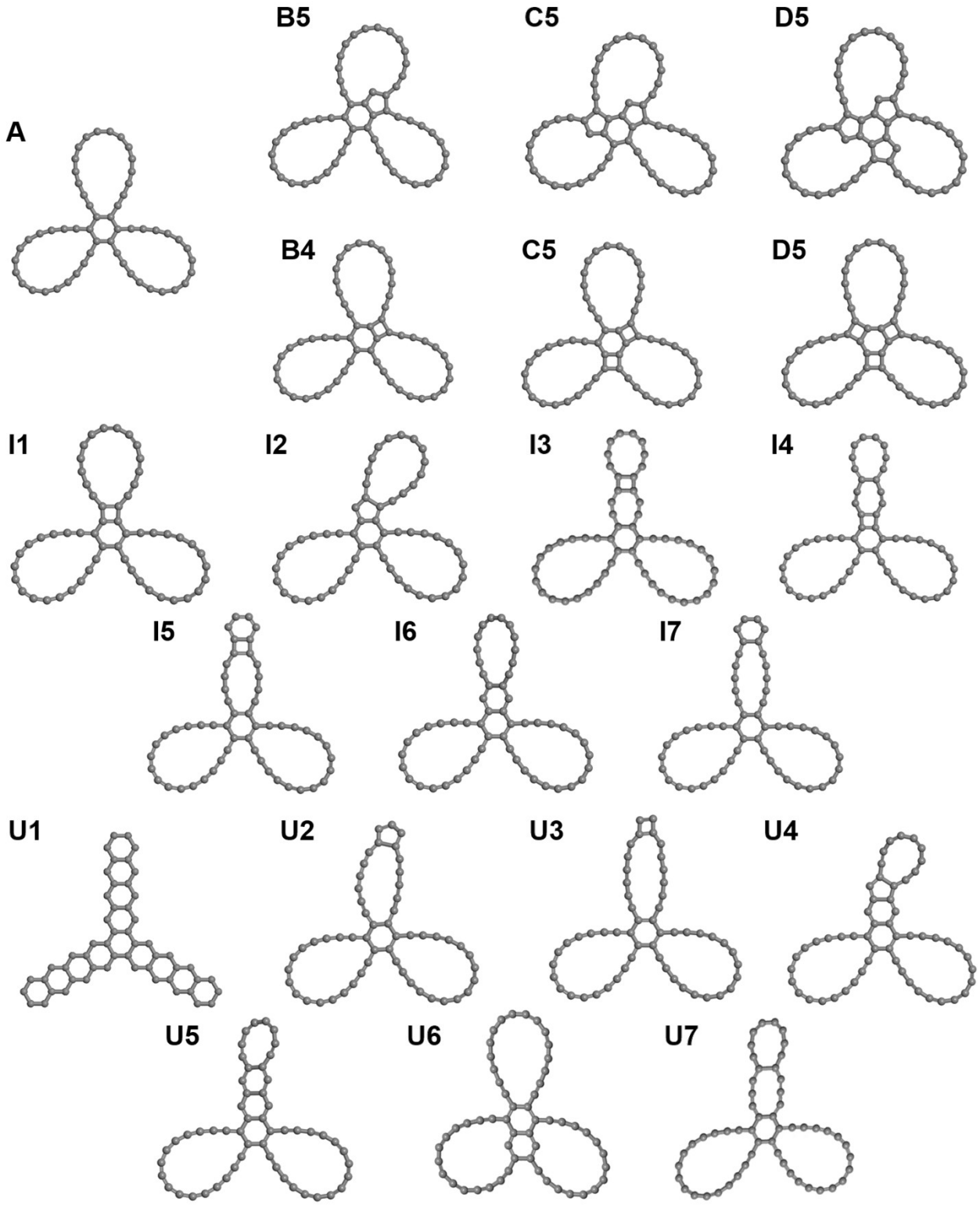


Figure S4. Molecules based on the carbon propeller-like molecule A (CPLM A) with additional bonds within and between atomic chains: molecules with bonds between the first atoms of neighbor atomic chains of the CPLM (B4-D4), molecules with bonds the first and second atoms (B5-D5), molecules with additional bonds within atomic chains metastable according to the DFT calculations (I1-I7) and molecules with additional bonds within and between atomic chains that are unstable according to the DFT calculations (U1-U7).

Table S1. Energies (in eV) of the molecules based on the carbon propeller-like molecule (CPLM) relative to the CPLM A obtained by the DFT calculations and calculations using the potentials REBO-1990EVC_CH and REBO-2002.

Molecule	DFT (PBE)	REBO-1990EVC_CH	REBO-2002
B4	0.58	1.03	1.05
B5	1.17	1.01	0.24
C4	0.71	2.30	2.02
C5	2.00	1.97	0.29
D4	0.31	3.59	3.00
D5	2.50	2.89	0.13
I1	0.89	1.28	1.30
I2	1.35	1.04	0.38
I3	1.95	3.17	1.43
I4	2.29	3.51	1.60
I5	2.96	4.80	2.33
I6	3.15	1.94	0.07
I7	3.15	3.27	0.91
U1	Unstable / 26.82 if fixed	23.34	4.07
U2	Unstable	Unstable	2.19
U3	Unstable	5.46	4.04
U4	Unstable	3.34	0.64
U5	Unstable	Unstable	0.41
U6	Unstable	1.78	-0.37
U7	Unstable	1.86	-0.01

Table S2. Barriers (in eV) for the transitions between the carbon propeller-like molecule A (CPLM A) and the molecules with bonds between the first atoms (B4-D4) and the first and second atoms (B5-D5) of neighbor atomic chains of the CPLM obtained via the DFT calculations and using the potentials REBO-1990EVC_CH and REBO-2002.

Reaction	DFT (PBE)	REBO-1990EVC_CH	REBO-2002
A -> B4	0.73	1.18	1.62
A -> B5	1.41	2.46	1.98
B4 -> C4	1.11	3.76	2.57
B5 -> C5	2.23	1.31	2.12
C4 -> D4	0.95	2.21	3.70
C5 -> D5	2.72	3.14	1.88

References

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